

# Bioinorganic Chemistry of Metals Related to Photosynthesis

Yi Hu<sup>1, 2, 3, 4, \*</sup>

<sup>1</sup> Shaanxi Land Engineering Construction Group Co., Ltd., China

<sup>2</sup> Institute of Land Engineering and Technology, Shaanxi Land Engineering Construction Group Co., Ltd., China

<sup>3</sup> Key Laboratory of Degraded and Unused Land Consolidation Engineering, the Ministry of Natural Resources, China

<sup>4</sup> Shaanxi Provincial Land Consolidation Engineering Technology Research Centre, Xi'an, 710075, China

\* Corresponding author Email: 490234215@qq.com

**Abstract:** Many inorganic elements play fundamental role in biochemical processes, such as photosynthesis, which is an incredibly important biological processes in this planet. This paper reviewed the role of Mg, Mn, Cu and Fe in photosynthesis. Magnesium plays a role in maintaining the structure of chlorophyll, due to its appropriate size, charge, and redox-inert feature. Manganese is required for photosynthetic O<sub>2</sub> evolution. Copper and iron usually form metalloproteins with ligands such as halide and amino acid residual and serve as electron transporters in PSI and PSII. In the past a couple of decades, structures of major redox metalloproteins and principles of important photosynthetic reactions have been intensively studied, and significant progresses have been made. However, there are still a number of ambiguous points that need to be clarified.

**Keywords:** Photosynthesis; Chlorophyll; O<sub>2</sub> Evolution; Electron Transfer.

## 1. Introduction

The term “Bioinorganic Chemistry” seems to involve a contradiction, because traditional biochemistry primarily cares about organic compounds. However, great advances in analytical methods (e.g., NMR) in the past a few decades have demonstrated the fundamentality of many “inorganic” elements in biochemical processes. Therefore, the rapidly developing field of bioinorganic chemistry mainly focuses on the role of inorganic chemicals (e.g., metal ions and metal compounds) in biological structures and functions.

Photosynthesis is an incredibly important biological processes in this planet. A diverse group of living organisms, for example, cyanobacteria and higher plants, harvest solar energy and convert it to chemical potential, assimilate carbon dioxide to make carbohydrates, and oxidize water to molecule dioxygen. These photosynthetic reactions make tremendous contribution to keeping a sustainable biosphere. Certain main group metals (e.g., Mg and Ca) and transition metals (e.g., Mn, Fe, Cu, and Zn) are involved in different structures and reactions of photosynthesis, because of their distinct redox potential, coordination geometry, and consequently specific functions [1]. Therefore, the objective of this paper is to briefly review the key features of Mg, Mn, Fe, and Cu

concerning their role in plant photosynthesis.

## 2. Role of Mg in Chlorophyll Structure and Function

Magnesium-containing chlorophyll is the primary pigment for light capture in plant cells. Magnesium (II) is a hard Lewis acid and prefers octahedral coordination when the oxygen donors are present (e.g., H<sub>2</sub>O); however, binding of Mg to the macrocyclic ring of the chlorophyll molecule is uncommon. The four N-donors from the porphyrin ring are on the same plane (Fig. 1a), but further binding to the ring through another N-donor from histidine imidazole is more or less out of the plane (Fig. 1b) [2]. This five-coordinated complex may be stable to hydrolysis since the Mg (II) ion is encapsulated by the porphyrin ring and attached amino acid.

It is intriguing to investigate why chlorophyll employ Mg (II) instead of other metal ions. The characteristics of Mg (II) ion could suggest an answer. The captured energy by chlorophyll will be further transported to the “reaction center” in the chloroplast via special arrangement of the light-harvest pigment. The process requires no mass or charge exchange, and Mg makes contribution to maintaining this well-designed spatial orientation [2, 3].

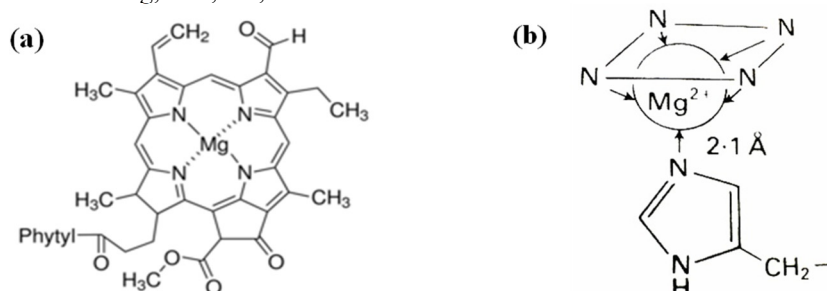
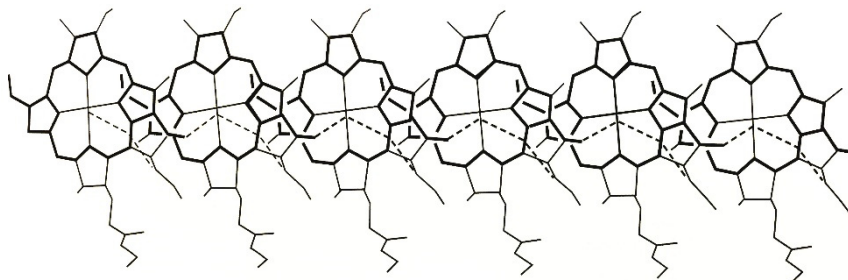


Fig 1. (a) The structure of chlorophyll b (b) the binding of histidine to the Mg of chlorophyll [2]

Aggregation of a chlorophyll derivative with ethyl side groups in the cyclopentanone ring is demonstrated in Fig. 2. The nucleophilic carbonyl

groups in the cyclopentanone ring interact with the coordinately unsaturated Mg (II) centers of adjacent

chlorophyll molecules through hydrogen-bond offered by water molecules, which allows the precise organization of those molecules [4]. Magnesium is the only main group metal ion that is naturally abundant in the earth and has the appropriate size and charge for the porphyrin ring of



**Fig 2.** Structure of a one-dimension aggregate occurring in the crystals of ethyl chlorophyllide dehydrate [6]. The  $\pi$  electron conjugation is represented by thick lines, and H-bond links via water molecules by broken lines

The redox inactivity of Mg (II) is another important property. Other small ions, such as Mn (II) and Fe (II) may fit in the porphyrin cavity, but those redox-active metals could enhance undesired heat or light production. Since metal centers like FeII/III could easily perform intramolecular electron transfer, intermolecular electron transfer will be prevented and consequently no or little chemical energy will be stored [7]. Therefore, the redox-inert Mg (II) ion is the only choice with regard to proper size and oxidation for porphyrin cavity and loss-free energy transfer.

### 3. Role of Mn in Oxidizing Water to Dioxygen Molecule

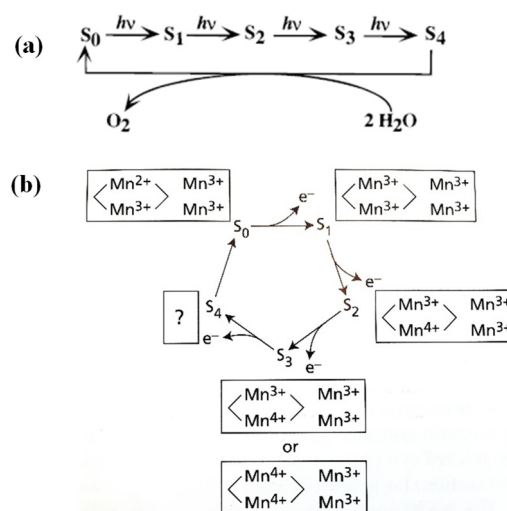
Manganese is a  $3d^5$  element and a redox-active transition metal with versatile oxidation states ranging from +2 to +7. In acidic aqueous solution, Mn (II) is the most stable species, but when oxygen is present or in alkaline solution, Mn (II) is quickly oxidized to a more stable Mn (IV). In plant photosynthesis, Mn is mainly required to form a tetranuclear Mn-cluster called the “oxygen-evolving complex (OEC)”. Water cleavage and  $O_2$  evolution occur with the help of the OEC. Water oxidation to  $O_2$  is very energy-demanding at acidic to neutral pH. Until now the oxygenic photosynthesis is the only known biochemical process that carries out this reaction spontaneously. This process has attracted much interest, and substantial effort has been devoted to unveiling the structure of the Mn-cluster and illuminating the underlying mechanisms. In the past 30 years, significant progresses have been achieved.

The first major breakthrough was reported by Joliot et al. in 1969 [8]. They exposed a sample of dark-adapted photosynthetic membrane to a sequence of very short yet intense flash and observed a unique pattern of oxygen production. Little or no oxygen was released on the first two flashes and the maximum yield of oxygen was on the third flash. This phenomenon repeated with a periodicity of four flashes.

To account for these results, a schematic model, called the “S state mechanism”, was proposed by Kok and colleagues in 1970s [9, 10]. This model comprises of a series of five states, defined as  $S_0$  to  $S_4$  (Fig. 3a). The  $S_4$  state reacts with two molecules of water to produce one molecule of  $O_2$  without further input of photons, thereafter, the  $S_0$  state is regenerated. The  $S_2$  and  $S_3$  states rapidly decay to the  $S_1$  state in the absence of light, which is stable in the dark. In addition, the  $S_0$  state is quickly oxidized to the  $S_1$  state with a half time of

chlorophyll [5, 6]. Heavier main group metals have higher spin-orbit coupling constant, and could trigger an intersystem crossing [2], leading to eventually reduced turnover rate of the photosynthetic reactions.

10 min at room temperature [11]. This model perfectly explains the observed pattern of  $O_2$  production but provides no information for the chemical nature of the S states. Followed studies using X-ray absorption [12] and EPR [13] have demonstrated that Mn is oxidized in the  $S_0$  to  $S_3$  transitions. The Mn (II) ion is oxidized to Mn (III) from the  $S_0$  to  $S_1$  transition, and one of the Mn (III) ions is further oxidized to Mn (IV) in the  $S_2$  state [14] as shown in Fig. 3b. The oxidation states of  $S_3$  and  $S_4$  remain unresolved until recently. Siegbahn [15, 16] suggests that one more Mn (III) is oxidized to Mn (IV) from the  $S_2$  to the  $S_3$  state, and a terminal oxygen on one of the Mn (IV) ions, instead of the Mn ion itself, is oxidized in the  $S_3$  to  $S_4$  transition.



**Fig 3.** (a) The S state model prepared by Kok and coworkers [9] (b) Possible scheme for the redox states of the water-oxidizing Mn cluster [12]

The coordination chemistry of the Mn-cluster in each S intermediate has been extensively studied since 1980s. Dismukes and Siderer [17] first observed a multiline EPR signal of  $S_2$  state from spinach chloroplast, indicating the presence of a multinuclear Mn site, either binuclear or tetranuclear. Subsequent studies using extended X-ray absorption edge fine structure (EXAFS) [18, 19, 20] demonstrated a 2.7-Å Mn-Mn distance in the  $S_2$  state and a longer 3.3-Å Mn-Mn distance in the  $S_1$  state. These evidence supports existence of an exchange-coupled tetranuclear Mn complex. However, the exact structure of the Mn complex

remained uncertain until about 10 years ago. With the assistance of the theory and experimental methods of quantum chemistry, the first X-ray 3D structure of Mn-cluster from cyanobacteria *Thermosynechococcus elongatus* was determined at a resolution of about 3.5 Å by Ferreira et al. [21] in 2004 and at 3.0 Å by Loll et al. [22] in 2005. The two proposed structures are mostly the same with a few distinguishable characteristics. The structure reported by Ferreira et al. [21] suggested that three Mn ions of the Mn-cluster and a Ca<sup>2+</sup> ion forms a cubane-like structure (Mn<sub>3</sub>CaO<sub>4</sub>), whereas the fourth Mn ion is connected to the cubane through mono-μ-oxo bridges provided by one of the oxo groups. The 3.0 Å model [22] did not incorporate the oxo bridges into the structure. Furthermore, the electron density that was assigned to the bicarbonate ion by Ferreira et al. [21] was not observed by the 3.0 Å model [22]. Subsequent study [23] by a higher resolution (1.9 Å) X-Ray indicated that the five metal atoms are interlinked via μ-oxo bridges supplied by five oxygen atoms. Four water molecules, possibly served as substrate for dioxygen production are also attached to the Mn<sub>4</sub>CaO<sub>5</sub> cluster. Different amino acid residuals are also coordinated towards the Mn<sub>4</sub>CaO<sub>5</sub> cluster, which helps making the ligand environment saturated (e.g., each Mn is hexacoordinated) [23]. The Ca-O bond at the corner of the cubane is 2.7 Å, which is longer relative to the Ca-O bond in the cubane (2.4–2.5 Å). Similarly, the Mn-O bond at the corner (2.4–2.6 Å) is longer than the Mn-O bond in the cubane (1.8–2.1 Å). These varied bond length data indicate that the Mn<sub>3</sub>CaO<sub>4</sub> cubane-like structure is asymmetrical [24].

Yruela [1] argued that those structure data obtained from cyanobacteria are not applicable to higher plants, possibly due to the heterogeneity of the photosynthetic system in higher plants. Furthermore, a recent study [24] has pointed out that previously reported models and structures are actually a mixture of varied intermediate states due to inevitable radiation reduction. A highly reduced S-3 intermediate, Mn (II, II, III, III), makes the greatest (about 60%) contribution [24]. This situation brings extra difficulty to interpretation of the obtained structure data. Until now, no 3D structure of Mn cluster in higher plants has been resolved.

Despite of these concerns, interpretation of currently available structural data has considerably helped to elucidate the underlying mechanisms of photosynthetic O<sub>2</sub> production. A couple of mechanisms have been proposed. The popular “2+2” mechanism was originally reported by Hoganson and Babcock [25]. This mechanism assumes that two sets of Mn dimer that are very close to each other exist in the oxygen evolving complex, and one water molecule is attached to each dimer. The two water molecules are progressively oxidized to form a Mn-oxo group on one dimer and a hydroxyl group on the other, thereafter one more proton is removed and an unstable peroxy species between the dimers is formed. This intermediate then quickly decayed and O<sub>2</sub> is produced [25]. This mechanism has become less favorable in recent years because the hypothesis of two Mn dimers is contradictory to the latest structural findings [21, 22, 23, 24]. In view of those recently reported structures, a modification to the “2+2” mechanism was developed. The key points of this mechanism include formation of a highly-oxidized Mn-oxo radical group that is subject to nucleophilic attack by a nearby water or hydroxyl group. A major debate concerning this mechanism focuses on the nature of the high-valent Mn-oxo group. Since Mn (V)-oxo has never been observed in previous studies using spectroscopy, Siegbahn [26] presumes that Mn (IV)-

oxyl may be the actually active species. Due to the limitations of current technology, it is almost impossible to distinguish between these two species. Again, current contention over possible mechanisms have not reached consensus. A leap in theory and experimental technology may facilitate the progress.

Scientists have been trying to synthesize robust catalysts that could efficiently drive the water oxidation reaction, and a few trailblazing advances have been reported. Homogenous water oxidation was first achieved via a ruthenium dimer, [(bpy)<sub>2</sub>(H<sub>2</sub>O)Ru<sup>III</sup>ORu<sup>III</sup>(H<sub>2</sub>O)(bpy)<sub>2</sub>]<sup>4+</sup> prepared by Gersten et al. [27] in early 1980s. Upon addition of 4 equiv of Ce (IV) to 0.01 M HClO<sub>4</sub> solution containing trace amount of the Ru (III) dimer, O<sub>2</sub> rapidly appears. However, addition of excessive Ce (IV) could destroy the catalytic ability of the system, possibly due to the decomposition of the dimer structure. Ruthenium is a second-row transition metal and has a very slow ligand exchange rate, therefore isotopic composition of evolved oxygen has been used to determine the mechanism of oxygen evolution. After the Ru (III) dimer was enriched with <sup>18</sup>O at the cis-aqua positions and further oxidized in unlabeled aqueous solutions, Yamada et al. [28] found that the evolved O<sub>2</sub> is predominantly <sup>18</sup>O<sup>16</sup>O, and little <sup>16</sup>O<sup>16</sup>O and <sup>18</sup>O<sup>18</sup>O are produced. These results indicate that the evolution of O<sub>2</sub> includes a single oxo group attached to Ru and a water molecule from the solvent.

In addition to the ruthenium complexes, Mn complexes that resemble the oxygen-evolving center also attract great interest. The first Mn-based homogeneous water-oxidation catalyst is [(terpy)(H<sub>2</sub>O)Mn<sup>III</sup>(O)<sub>2</sub>Mn<sup>IV</sup>(OH<sub>2</sub>)(terpy)]<sup>3+</sup> (terpy= 2,2': 6', 2''-terpyridine) prepared by Limburg et al. [29, 30]. This Mn dimer catalyze O<sub>2</sub> evolution when oxygen donors such as NaClO or KHSO<sub>5</sub> are present in the aqueous solution. Unlike ruthenium complex, the Mn dimer does not generate O<sub>2</sub> in aqueous solution when using Ce (IV) as an oxidant. This is because the Mn dimers decompose to MnO<sup>4-</sup> ions when the Ce (IV) oxidant is present [31]. However, the reaction of Mn dimer with a Ce (IV) oxidant for O<sub>2</sub> evolution may occur if the Mn dimer is adsorbed on layer compounds such as kaolin [31] and montmorillonite K10 [32]. To date, the mechanism of the Mn dimer catalyzed O<sub>2</sub> evolution is still unclear.

In sum, tremendous efforts have been endeavored to decoding the mysterious structure of oxygen evolving complex and the underlying mechanism of O<sub>2</sub> evolution. Despite numbers of trailblazing breakthrough has been achieved in the past two decades, the truth is still in the dark, and painstaking effort is still required before the dawn.

## 4. Role of Cu in Photosynthetic Electron Transfer

Copper is a 3d<sup>10</sup> element and a redox-active transition metal that can exist as Cu (I) and Cu (II). In chloroplast, it is required to form plastocyanin (Pc), which is an electron carrier in primary photosynthetic reactions. Copper in the stroma also serves as a constituent of Cu/Zn superoxide dismutase (SOD), a strong reductant that could efficiently quench reactive oxygen species and protect the chloroplast membrane [1].

Plastocyanin belongs to the blue copper protein family. A distinct feature of this soluble protein is its dark blue color caused by intensive electronic absorption at about 600 nm. This intensity may be explained by the ligand-to-metal electron transfer. Upon light excitation, one electron will be

transferred to the electron-poor Cu (II) center from the thiolate ligand, which is a strong  $\sigma$  donor [33]. In ground state, it has been estimated that an especially strong  $\pi$  bond exists between the  $d_{x^2-y^2}$  orbital of Cu (II) ion and the p orbital of S ion from cysteine, and the unpaired electron is almost equally shared between the two orbitals [34]. In this situation, the redox center of plastocyanin actually behaves as  $\text{Cu}^{1.5+}$  and  $\text{S}^{1.5-}$ .

Crystal structure of isolated plastocyanin was first determined in spinach [35]. The Cu (II) ion has a  $d^9$  configuration, and the unpaired electron in the eg orbital leads to a significant Jahn-Teller distortion, which is clearly shown in Fig.4. The two N atoms from histidine residuals and the S atom from cysteine are tightly bound in a trigonal plane. The other S provided by methionine forms weak bond with Cu (II) on the axial position [35]. This is trigonal pyramidal coordination contributes to the high midpoint redox potential (about 370 mV at pH 7) and the relatively low relaxation energy related to the redox process [1].

The scheme of electron transfer through plastocyanin has been resolved. The Cu (II) ion is first reduced to Cu (I) by the cytochrome b6f complex, then the reduced Cu (I) donates one electron to the photo-excited PSI. The turnover rate of CuI/II is very fast, which enables efficient energy transport. This process is regulated by divalent cations such as  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  and is pH-dependent [1].

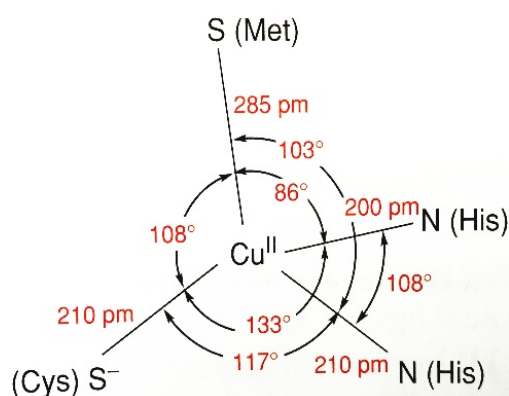


Fig 4. Crystal structure of active site of plastocyanin containing Cu (II) from spinach leaves [35]

## 5. Role of Fe in Photosynthetic Electron Transfer

Iron is the fourth abundant element in the earth's crust. Similar to Cu and Mn, Fe is also a redox-active metal that is able to exist as Fe (II) and Fe (III). Uptake of Fe (II) is preferred by higher plants. It has long been known that Fe deficiency could adversely affect the photosynthetic ability of higher plants, because Fe plays key role in chloroplast structure and electron transfer. A significant number of electron-transfer proteins use Fe-S clusters as redox center. Mononuclear rubredoxin and multinuclear ferredoxins, such as  $[2\text{Fe}-2\text{S}]$  and  $[4\text{Fe}-4\text{S}]$  have been extensively studied. Structures [5] of some Fe-S clusters are illustrated in Fig. 5.

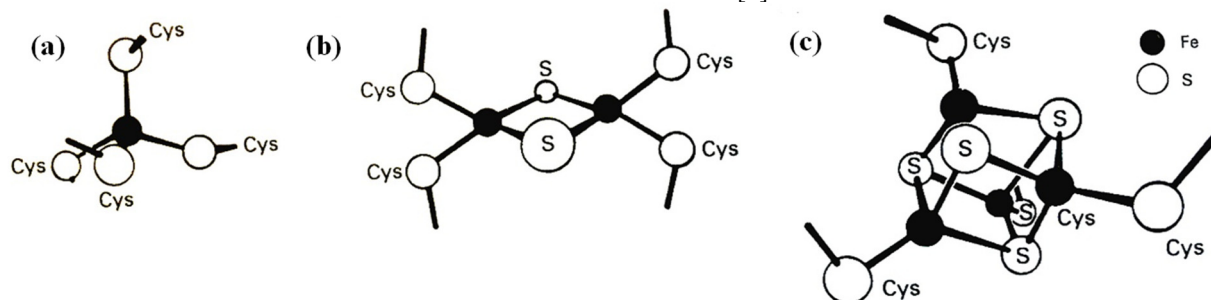


Fig 5. The coordination of Fe-S proteins (a) rubredoxin (b)  $\text{Fe}_2\text{S}_2$  ferredoxin (c)  $\text{Fe}_4\text{S}_4$  ferredoxin [5]

Rubredoxins are bacterial proteins of low molecular weight, containing only one Fe ion. The sulfur ions from four cysteine groups are arranged in a distorted tetrahedral coordination (Fig. 5a). The redox potential of rubredoxin ranges from 0 to 100 mV, but until now, little is known about the physiological electron donors and acceptors of rubredoxins. Study [37] has shown that some bacteria are capable of conducting alkanes and arenes assimilation using  $[2\text{Fe}-2\text{S}]$  ferredoxins instead of the monomers. This finding suggests dimeric redox centers are possibly required for biological function.

In chloroplast of higher plants, Fe is an important constituent of the chlorophyll-binding membrane protein complex in PSI. The X-ray 3D structure of PSI from pea [38] revealed that each PSI monomer has three  $[4\text{Fe}-4\text{S}]$  clusters denoted as FA, FB, and FX, and one  $[2\text{Fe}-2\text{S}]$  ferredoxin. Ferredoxin is the first soluble acceptor of electrons on the stromal side of the electron transport chain in the chloroplast. The 3D structure of ferredoxin from pea reveals that this protein consists of a fold featuring a four-stranded  $\beta$ -sheet with an  $\alpha$ -helix packed across its face [38]. Out of the three  $[4\text{Fe}-4\text{S}]$  clusters, FX attracts more interests than FA and FB due to its unique structure and function. This interpolypeptide

cluster bridges the PsaA and PsaB subunits of PSI to form a heterodimeric reaction center, which catalyzes the light-induced primary charge separation at the chlorophyll a. Each of the two subunits provides two cysteine ligands coordinating to the Fe center. This unique symmetrical coordination is necessary for subsequent binding of PsaC subunit [39]. The interactions among amino acid residuals also make FX one of the most electronegative Fe-S clusters.

Since no other MnSn clusters have been found in living organisms, an interesting question that needs to be answered is why the  $\text{Fe}_n\text{S}_n$  cluster is chosen over some other metal cluster. To date, no scientific basis has been reported. One hypothesis suggests that in ancient times, Fe and S are the only available elements that could efficiently provide energy to the earliest forms of life [5].

Many cofactors in PSII are comprised of Fe; therefore, Fe deficiency could lower the efficiency of photochemical conversion. The non-heme Fe is located in the stromal side of the intermembrane protein and adopts a pseudooctahedral ligand geometry. Four of the coordination sites are occupied by histidine residuals, while exogenous bidentate bicarbonate fills the rest two sites [40]. Even though binding sites have

been deciphered, functions of those non-heme Fe are not fully understood. Current study suggests that non-heme Fe may have a role in regulating proton-coupled electron-transfer reactions of quinone acceptors [41].

One example of heme-protein is cytochrome  $b_{559}$ . The  $\alpha$ - and  $\beta$ -subunits of this protein are linked through a heme-bridge. Two histidine residues of the  $\alpha$ - and  $\beta$ -subunits are coordinated to the heme Fe as axial ligands [42]. Among all the b-type cytochromes,  $\text{cyt } b_{559}$  is the only one that has singular redox potential and several midpoint redox potential forms [1]. Another example of Fe-containing protein is the cytochrome complex ( $\text{cyt } b_6f$ ), which serves as an electronic bridge linking the PSI and PSII reaction centers. The  $\text{cyt } b_6f$  complex of higher plants comprises of four Fe redox cofactors [43], including the heme of  $\text{cyt } f$ , the Rieske protein, which is a  $[\text{Fe}_2\text{S}_2]$  cluster with high redox potential, and the two b hemes ( $b_n$  and  $b_p$ ), which are constituents of  $\text{cyt } b_6$ . One additional subunit, named ferredoxin-NADP<sup>+</sup> reductase (FNR), was isolated from  $\text{cyt } b_6f$  complex of spinach thylakoid membranes [44], but existence of this subunit in other higher plants has not been proven.

## 6. Summary

Living organisms have evolved the capacity to use inorganic elements for key biological processes. Many main group and transition metals are actively involved in photosynthesis. Magnesium plays a role in maintaining the structure of chlorophyll, due to its appropriate size, charge, and redox-inert feature. Manganese is required for photosynthetic O<sub>2</sub> evolution. Copper and iron usually form metalloproteins with ligands such as halide and amino acid residual and serve as electron transporters in PSI and PSII.

In the past a couple of decades, structures of major redox metalloproteins and principles of important photosynthetic reactions have been intensively studied, and significant progresses have been made. However, there are still a number of ambiguous points that need to be clarified.

## Acknowledgments

The authors gratefully acknowledge the financial support from XXX funds.

## References

- [1] Yruela I. Transition metals in plant photosynthesis. *Metallomics*, 2013, 5(9): 1090-1109.
- [2] Kaim W, Schwederski B, Klein A. *Bioinorganic Chemistry--Inorganic Elements in the Chemistry of Life: An Introduction and Guide* (Second edition). West Sussex: John Wiley & Sons, 2013.
- [3] Deisenhofer J, Michel, H. The Photosynthetic reaction center from the purple bacterium *Rhodospseudomonas viridis* (Nobel Lecture). *Angewandte Chemie International Edition in English*, 1989, 28(7): 829-847.
- [4] Chow H C, Serlin R, Strouse C E. Crystal and molecular structure and absolute configuration of ethyl chlorophyllide a-dihydrate. Model for the different spectral forms of chlorophyll a. *Journal of the American Chemical Society*, 1975, 97(6): 7230-7237.
- [5] Silva J J R F, Williams R J P. *The biological chemistry of the elements: the inorganic chemistry of life* (Second Edition). New York: Oxford University Press Inc, 2001.
- [6] Sigel H, Sigel A. *Metal ions in biological systems*. Boca Raton: CRC Press, 1990.
- [7] Marcus R A. *Electron transfer reactions in chemistry: Theory and experiment* (Nobel Lecture). *Angewandte Chemie International Edition in English*, 1993, 32(8): 1111-1121.
- [8] Joliet P, Barbieri G, Chabaud R. Un nouveau modele ds centres photochimiques du systeme II. *Photochemistry and Photobiology*, 1969, 10(5): 309-329.
- [9] Kok B, Forbush B, McGloin M. Cooperation of charges in photosynthetic O<sub>2</sub> evolution-I. A linear four step mechanism. *Photochemistry and Photobiology*, 1970, 11(6): 457-475.
- [10] Forbush B, Kok B, McGloin P. Cooperation of charges in photosynthetic O<sub>2</sub> evolution-II. Damping of flash yield oscillation, deactivation. *Photochemistry and Photobiology*, 1971, 14(3): 307-321.
- [11] Brudvig G W, Crabtree R H. *Bioinorganic chemistry of manganese related to photosynthetic oxygen evolution*. *Progress in Inorganic Chemistry*, 1989, 37: 99-142.
- [12] Dismukes G C, Siderer Y. Intermediates of a polynuclear manganese center involved in photosynthetic oxidation of water. *PNAS*, 1981, 78(1): 274-278.
- [13] Goodin, D B, Yachandra VK, Britt R D, Sauer K, Klein M P. The state of manganese in the photosynthetic apparatus. 3. Light-induced changes in X-ray absorption (K-edge) energies of manganese in photosynthetic membranes. *Biochimica et Biophysica Acta-Bioenergetics*. 1984, 767(2): 209-216.
- [14] Rutherford A W, Zimmerman J L, Boussac A. *The photosystems: Structure, Function and molecular biology* (topics in Photosynthesis, vol.11), Amsterdam: Elsevier, 1993.
- [15] Siegbahn P E M. Mechanisms for proton release during water oxidation in the S<sub>2</sub> to S<sub>3</sub> and S<sub>3</sub> to S<sub>4</sub> transitions in photosystem II. *Physical Chemistry Chemical Physics*, 2012, 14: 4849-4856.
- [16] Siegbahn P E M. Water oxidation mechanism in photosystem II, including oxidations, proton release pathways, O-O bond formation and O<sub>2</sub> release. *Biochimica et Biophysica Acta-Bioenergetics*, 2013, 1827(8-9): 1003-1019.
- [17] Dismukes G C, Siderer Y. EPR spectroscopic observations of a manganese center associated with water oxidation in spinach chloroplasts. *FEBS letter*, 1980, 121(1): 78-80.
- [18] Yachandra V K, Guiles R D, McDermott A E, Britt R D, Sauer K, Klein M P. The state of manganese in the photosynthetic apparatus: 4. Structure of the manganese complex in Photosystem II studied using EXAFS spectroscopy. The S<sub>1</sub> state of the O<sub>2</sub>-evolving Photosystem II complex from spinach. *Biochimica et Biophysica Acta-Bioenergetics*, 1986, 850(2): 324-332.
- [19] Yachandra V K, Guiles R D, McDermott A E, Britt R D, Dexheimer S L, Sauer K, Klein M P. The S<sub>0</sub> state of photosystem II induced by hydroxylamine: differences between the structure of the manganese complex in the S<sub>0</sub> and S<sub>1</sub> states determined by X-ray absorption spectroscopy. *Biochemistry*. 1987, 26(2): 5974-5981.
- [20] George G N, Prince R C, Cramer S P. The manganese site of the photosynthetic water-splitting enzyme. *Science*, 1989, 243(4892): 789-791.
- [21] Ferreira K N, Iverson T M, Maghlaoui K, Barber J, Iwata S. Architecture of the photosynthetic oxygen-evolving center. *Science*, 2004, 303(5665): 1831-1838.
- [22] Loll B, Kern J, Saenger W, Zouni A, Biesiadka J. Towards complete cofactor arrangement in the 3.0 Å resolution structure of photosystem II. *Nature*, 2005, 438(7070): 1040-1044.
- [23] Umena Y, Kawakami K, Shen J R, Kamiya N. Crystal structure of oxygen-evolving photosystem II at a resolution of 1.9 Å. *Nature*, 2011, 473(7345): 55-60.

- [24] Galstyan A, Robertazzi A, Knapp E W. Oxygen-evolving Mn cluster in photosystem II: the protonation pattern and oxidation state in the high-resolution crystal structure. *Journal of the American Chemical Society*, 2012, 134(17): 7442-7449.
- [25] Hoganson C W, Babcock G T. A metalloradical mechanism for the generation of oxygen from water in photosynthesis. *Science*, 1997, 277(5334): 1953.
- [26] Siegbahn P E M. O-O bond formation in the S(4) state of the oxygen-evolving complex in photosystem II. *Chemistry A European Journal*, 2006, 12(36): 9217-9227.
- [27] Gersten S W, Samuels G J, Meyer T J. Catalytic oxidation of water by an oxo-bridged ruthenium dimer. *Journal of the American Chemical Society*, 1982, 104(14): 4029-4030.
- [28] Yamada H, Siems W F, Koike T, Hurst J K. Mechanisms of water oxidation catalyzed by the *cis,cis*-[(bpy)<sub>2</sub>Ru(OH<sub>2</sub>)<sub>2</sub>O<sup>4+</sup> ion. *Journal of the American Chemical Society*, 2004, 126(31): 9786-9795.
- [29] Limburg J, Vrettos J S, Liable-Sands L M, Rheingold A L, Crabtree R H, Brudvig G W. A functional model for O-O bond formation by the O<sub>2</sub>-evolving complex in photosystem II. *Science*, 1999, 283(5407): 1524-1527.
- [30] Limburg J, Vrettos J S, Chen H Y, Paula J C, Crabtree R H, Brudvig G W. Characterization of the O(2)-evolving reaction catalyzed by [(terpy)(H<sub>2</sub>O) Mn(III)(O) 2Mn (IV) (OH<sub>2</sub>) (terpy)] (NO<sub>3</sub>)<sub>3</sub> (terpy = 2,2':6,2''-terpyridine). *Journal of the American Chemical Society*, 2001, 123(3): 423-430.
- [31] Yagi M, Narita K, Catalytic O<sub>2</sub> evolution from water induced by adsorption of [OH<sub>2</sub>) (terpy)Mn(mu-O)<sub>2</sub>Mn(terpy)(OH<sub>2</sub>)]<sup>3+</sup> complex onto clay compounds. *Journal of the American Chemical Society*, 2004. 126(26): 8084-8085.
- [32] Yagi M; NaritaK, Maruyama S, Sone K, Kuwabara T, Shimizu K I. Artificial model of photosynthetic oxygen evolving complex: catalytic O<sub>2</sub> production from water by di-mu-oxo manganese dimers supported by clay compounds. *Biochimica et Biophysica Acta-Bioenergetics*, 2007, 1767(6): 660-665.
- [33] Solomon E I, Baldwin M J, Lowery M D. Electronic structures of active sites in copper proteins: Contributions to reactivity. *Chemical Reviews*, 1992, 92(4): 521-542.
- [34] Holm R H, Kennepohl P, Solomon E I. Structural and Functional Aspects of Metal Sites in Biology. *Chemical Reviews*, 1996, 96(7), 2239-2314.
- [35] Xue Y, Okvist M, Hansson O, Young S. Crystal structure of spinach plastocyanin at 1.7 Å resolution. *Protein Science*. 1998, 7(10): 2099-2105.
- [36] Hope A B. Electron transfers amongst cytochrome f, plastocyanin and photosystem I: kinetics and mechanisms. *Biochimica et Biophysica Acta-Bioenergetics*, 2000, 1456(1): 5-26.
- [37] Mason J R, Cammack R. The electron-transport proteins of hydroxylating bacterial dioxygenases. *Annual Review of Microbiology*, 1992, 46: 277-305.
- [38] Ben-Shem A, Frolov F, Nelson N. Crystal structure of plant photosystem I. *Nature*, 2003, 426(6967): 630-635.
- [39] Nelson N, Ben-Shem A. Photosystem I reaction center: past and future. *Photosynthesis Research*, 2002, 73(1-3): 193-206.
- [40] Hienerwadel R, Berthomieu C. Bicarbonate binding to the non-heme iron of photosystem II investigated by Fourier transform infrared difference spectroscopy and <sup>13</sup>C-labeled bicarbonate. *Biochemistry*, 1995, 34(50): 16288-16297.
- [41] Ishikita H, Knapp E. Oxidation of the non-heme iron complex in photosystem II. *Biochemistry*, 2005. 44(45): 14772-14783.
- [42] Widger W R, Cramer W A, Hermodson M, Herrmann R G. Evidence for a hetero-oligomeric structure of the chloroplast cytochrome b-559. *FEBS Lett*. 1985, 191(2): 186-190.
- [43] Allen J F. Cytochrome b6f: structure for signalling and vectorial metabolism. *Trends in Plant Science*, 2004, 9(3): 130-137.
- [44] Zhang H, Whitelegge J P, Cramer W A. Ferredoxin: NADP<sup>+</sup> oxidoreductase is a subunit of the chloroplast cytochrome b6f complex. *Journal of Biological Chemistry*. 2001, 276(41): 38159-38165.